

Mechanism of enhanced photocatalysis with polyhydroxy fullerenes

Vijay Krishna^{a,b}, David Yanes^{a,b}, Witcha Imaram^c, Alex Angerhofer^c,
Ben Koopman^{a,d}, Brij Moudgil^{a,b,*}

^a Particle Engineering Research Center, 205 Particle Science and Technology Building, P.O. Box 116135,
University of Florida, Gainesville, Florida 32611, USA

^b Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, USA

^c Department of Chemistry, University of Florida, Gainesville, Florida, USA

^d Department of Environmental Engineering Sciences, University of Florida, Gainesville, Florida, USA

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Abstract

Polyhydroxy fullerenes (PHF) have been applied for increasing the photocatalytic degradation rate of TiO₂. Scavenging of photo-generated electrons and therefore higher generation of hydroxyl radicals was hypothesized as the mechanism for the observed enhancement. The present study confirms the increase in generation of hydroxyl radicals with electron paramagnetic resonance (EPR) spectroscopy. The concentration of hydroxyl radicals generated by a mixture of TiO₂ and PHF was up to 60% greater than the concentration obtained without PHF. These results are consistent with the observed enhancement in dye degradation and microbial inactivation experiments. The current study also demonstrates that PHF can improve the photocatalytic activity of different TiO₂.

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1. Introduction

Photocatalysis for degradation of organic pollutants and inactivation of microorganisms has been widely researched with titanium dioxide as photocatalyst. The research has mainly focused on improving the efficacy of photocatalyst in ultraviolet-A (320–400 nm) as well as visible light. The research efforts for enhancing the photocatalysis can be broadly classified in two categories—enhancement by increased adsorption of organic pollutants (directly or indirectly) to TiO₂ and enhancement by improving the photocatalytic efficiency. The former approach mainly depends on utilization of adsorbents such as activated carbon, silica, clays and zeolites in conjunction with titanium dioxide particles [1–7]. By its nature this approach is pollutant specific since the adsorbent systems must be tailored to the organic compounds of interest. Furthermore, studies indicate that this approach does not enhance degradation of some pollutants [3,5].

Improvement of photocatalytic efficiency is a more general approach that should improve degradation of all pollutants, microbial as well as organic. The approach involves integration of metals or organic compounds with TiO₂ to scavenge photo-generated electrons. Metals such as silver, gold and platinum are either deposited on titanium dioxide particles by reduction of their salts and electron beam evaporation, or co-synthesized with titanium dioxide precursors [8–12]. Doping of metals has also been achieved with ion beam implantation [13]. Organic compounds, which can conduct electrons, are covalently conjugated to titanium dioxide particles for scavenging of photo-generated electrons. Carbon allotropes (carbon nanotubes and hydroxylated fullerenes) have also been employed to increase the photocatalytic degradation of organic pollutants and inactivation of microorganisms [14–16].

In contrast to the various enhancers reported above, utilization of polyhydroxy fullerenes (PHF) does not require additional unit operations for integration with TiO₂. PHF, a hydrophilic and non-toxic version of fullerenes, adsorbs onto titanium dioxide particles by electrostatic interactions [14]. Based on photocatalytic dye degradation experiments, the optimum ratio of PHF/TiO₂ increased the dye degradation rate

* Corresponding author. Tel.: +1 352 846 1194; fax: +1 352 846 1196.

E-mail address: bmoudgil@perc.ufl.edu (B. Moudgil).

by 70%, which is in the range achieved with the other enhancers. However, the concentration of PHF per unit weight of TiO_2 to achieve this degree of improvement is 10–100 times lower than other enhancers. Scavenging of photo-generated electrons by PHF and therefore increase in generation of hydroxyl radicals was hypothesized to be the mechanism for enhancement in photocatalysis.

The purpose of the present study is to verify enhanced hydroxyl radical formation as the mechanism of improved photocatalysis when PHF is integrated with TiO_2 . Electron paramagnetic resonance (EPR) was used for determining the concentration of hydroxyl radicals by spin trapping with 5,5-dimethyl-1-pyrroline N-oxide (DMPO). Additionally, the capability of PHF to increase the photocatalytic activity of two different photocatalysts, anatase and Degussa P25, was explored. Procion Red MX-5B was employed as a model aromatic pollutant and *Escherichia coli* was used as a model microbial contaminant.

2. Materials and methods

2.1. Synthesis of PHF

The procedure for synthesizing polyhydroxy fullerenes (PHF) was similar to Li et al. [17]. Briefly, 80 mg of fullerenes (95% C_{60} , BuckyUSA, Houston, TX) was added to 60 mL of benzene (HPLC grade, Fisher) and stirred for 30 min. Subsequently, 2 mL of 25 M NaOH and 0.3 mL tetrabutyl ammonium hydroxide (TBAH) were added and stirred for 4 h. The mixture was then allowed to phase separate for 15 min and the top clear phase was removed by decantation. The bottom phase was then stirred with additional 20 mL of deionized water for 27 h. The suspension was then passed through a Whatman 40 filter to remove the suspended solids. The filtrate was then concentrated in a vacuum oven at 60 °C for 24 h. The remaining brown wet solid was then washed three times by repeated centrifugations (at 3000 rpm \times g for 15 min) with 50 mL methanol each time and finally dried in vacuum at 60 °C for 24 h. The weight of the dried PHF obtained was 124 mg.

2.2. Characterization of PHF

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectrum of PHF powder was obtained on Thermo Electron Magna 760 spectrometer with KBr as background. The PHF was also analyzed with X-ray Photoelectron Spectroscopy (Kratos Analytical Surface Analyzer XSAM 800). Analysis of XPS C 1s peak for determining the carbon oxidation states was performed by curve fitting with Grams 7.01 software.

2.3. HR-TEM imaging of PHF- TiO_2 nanocomposite

Samples for high resolution transmission electron microscopy (HR-TEM) were prepared by sonicating 30 mg L^{-1} of TiO_2 suspension for one hour, followed by ten fold dilution of the suspension. The diluted suspension was again sonicated for

30 min and PHF was added to the suspension to give 3 mg L^{-1} of TiO_2 and 0.3 mg L^{-1} of PHF in the final suspension. A 10 μL drop of suspension was pipetted on top of TEM grid (Lacey carbon grids, EMS, Hatfield, PA) and allowed to dry overnight. The samples were imaged with field emission HR-TEM (JEOL 2010F) at 15 kV accelerating voltage. The PHF- TiO_2 ratio was chosen to be 100 times higher than that employed for photocatalysis experiments to increase the probability of detection of PHF on TiO_2 surface.

2.4. Culturing of *Escherichia coli*

E. coli C3000 was cultured for 24 h at 37 °C and harvested to give a stock solution according to the protocol of Rincon and Pulgarin [18]. *E. coli* was stored in deionized water at 4 °C for a maximum of 24 h.

2.5. Dye degradation experiments

Dye degradation experiments were carried out according to the protocol of Krishna et al. [14]. Briefly, 30 mg L^{-1} of TiO_2 (anatase 5 nm, Alfa-Aesar) suspension was sonicated for 30 min followed by addition of PHF and Procion red MX-5B dye (Fisher) at a concentration of 0.03 and 3 mg L^{-1} , respectively. The reaction mixture was transferred to a Petri dish and mixed using a magnetic stirrer, with irradiation by UVA lamps (Southern New England Ultra Violet Company, Branford, CT) at intensity of 86 W m^{-2} . Two 0.5 mL samples were collected every 15 min for one hour. The samples were then centrifuged twice at 10,000 \times g for 15 min and the supernatants were analyzed with UV-vis spectroscopy (Perkin-Elmer Lambda 800, Wellesley, MA). The peak heights at 512 and 538 nm were used to quantify dye concentrations. Semilog plots of dye concentrations were plotted to determine the pseudo-first-order degradation rate coefficients.

2.6. *Escherichia coli* inactivation

The photocatalytic inactivation experiments were conducted with Degussa P25. The photocatalyst suspension was prepared at a concentration of 30 mg L^{-1} and sonicated (Misonix Sonicator 3000, Farmingdale, NY) for one hour at 165 W. Subsequently 0.03 mg L^{-1} of PHF was added to 20 mL of the photocatalyst suspension followed by addition of 10 mL of stock *E. coli* suspension. Initial concentration of *E. coli* in the reaction mixture was 3.6×10^7 cfu mL^{-1} . The reaction mixture was stirred using a magnetic stirrer, with irradiation by UVA at intensity of 86 W m^{-2} . Three 0.333 mL samples were collected every 15 min for 1 h. The collected samples were then serially diluted with phosphate buffered saline. Appropriate dilutions were plated on tryptic soy agar and incubated at 37 °C for 20 h prior to counting. Semilog graphs of survival ratio (concentration of *E. coli* at any given time normalized with initial concentration) vs. time were plotted to determine the first-order inactivation rate coefficients and *D*-value (time required for one log reduction in linear region of the graph).

2.7. Electron paramagnetic resonance measurements

EPR experiments were carried out to investigate the radical generation capability of PHF-TiO₂ nanocomposite. EPR spectra were recorded at room temperature using a commercial Bruker Elexsys E580 spectrometer employing Bruker's high-Q cavity, ER 4123SHQE, and using quartz capillaries of approximately 1 mm × 2 mm (i.d. × o.d.). Spectral parameters were typically 100 kHz modulation frequency, 1 G modulation amplitude, 2 mW microwave power, 9.87 GHz microwave frequency, 20.48 ms time constant and 81.92 conversion time/point.

A photocatalyst-spin trap mixture was made up by combining 190 μL of photocatalyst suspension containing 30 mg L⁻¹ TiO₂ and 0.03 mg L⁻¹ of PHF with 10 μL of DMPO (Alexis) and 6 quartz capillaries were filled with the mixture. EPR spectra were obtained before and after a predetermined time of exposure of each tube to UVA lamps (13 W m⁻²). To quantify the concentration of hydroxyl radicals generated, the integrated peak area of the DMPO-OH• spectra was compared with the integrated peak area of a spectrum using 10 μM 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy radical (HTEMPO) (Fluka) at each UVA irradiation time [19]. Analysis and double integration of the spectra was performed with Grace, version 5.1.20, a public domain 2D-plotting and data analysis package released under the GNU public license [<http://plasma-gate.weizmann.ac.il/Grace/>].

EPR experiments were also carried out to investigate the radical generation capability of PHF alone. Procedure was same as described above except that TiO₂ was omitted from the reaction mixture. Control experiments with neither PHF nor TiO₂ present were performed in the dark and under UVA irradiation.

3. Results and discussion

3.1. FTIR and XPS analysis

The FTIR spectrum of PHF synthesized by alkali hydrolysis in the present study (Fig. 1) is similar to spectra

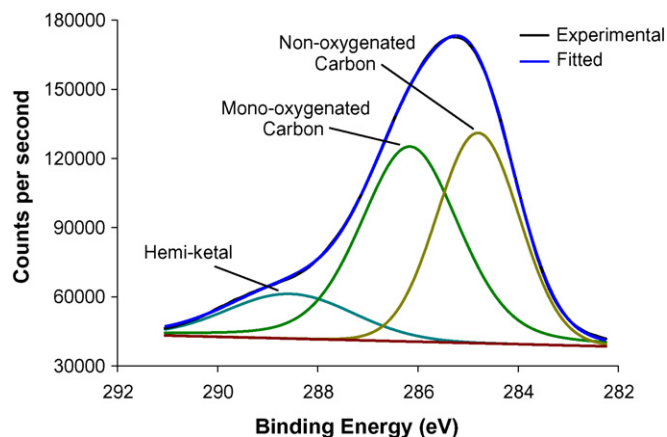


Fig. 2. Experimental C 1s XPS spectrum (top curve) of synthesized polyhydroxy fullerenes with fitted curves representing three different oxidation states of carbon.

obtained by researchers using either alkali hydrolysis [17,20–22] or acid hydrolysis [23]. The broad peak in the range of 3200 cm⁻¹ indicates the presence of hydrogen bonded hydroxyl groups [24]. The shoulder at 1658 cm⁻¹ is attributed to the presence of hemiketal structure [22]. The peak at 1594 cm⁻¹ is associated with C=C absorption. Peaks and shoulders at 1448, 1068 and 471 cm⁻¹ are associated with vibrations of C–O bonds [17,21].

XPS analysis of the PHF (full spectrum not shown) indicated the presence of C, O and Na at atomic concentrations of 61.23, 28.44 and 10.34%, respectively. The XPS C 1s region of the spectrum is shown as the top most peak in Fig. 2. Curve fitting analysis of the C 1s spectrum with three different oxidation states assigned to carbon [20] gave the following peaks: 284.8 eV (40.18% of the total area) assigned to non-oxygenated carbon, 286.16 eV (47.12%) assigned to hydroxylated carbon and 288.55 eV (12.69%) assigned to hemiketal carbon. Since no carbonyl peak was present in the FTIR spectrum, the highest oxidation state was assumed to be due to hemiketal structure as revealed from FTIR.

The composition of PHF in terms of C, O and Na as determined from the XPS spectrum and the relative carbon concentrations associated with hydroxyl, carbonyl and hemiketal functionalities were employed according to Husebo et al. [20] to deduce the molecular formula of PHF synthesized in the present study, giving C₆₀O₈(OH)₂₈Na₁₀. The number of functional groups added to the fullerene cage (36) in this study is within the range (24–42) of values reported by investigators using similar (alkali hydrolysis) functionalization methodology [20,21].

3.2. HR-TEM imaging of PHF-TiO₂ nanocomposite

HR-TEM images of PHF coated on TiO₂ are presented in Fig. 3. TiO₂ is in the form of agglomerates of 20–30 nm size. A single crystal size of 5 nm is apparent from other images (not shown). PHF is present as clusters of 2–3 nm with apparent lattice diffraction.

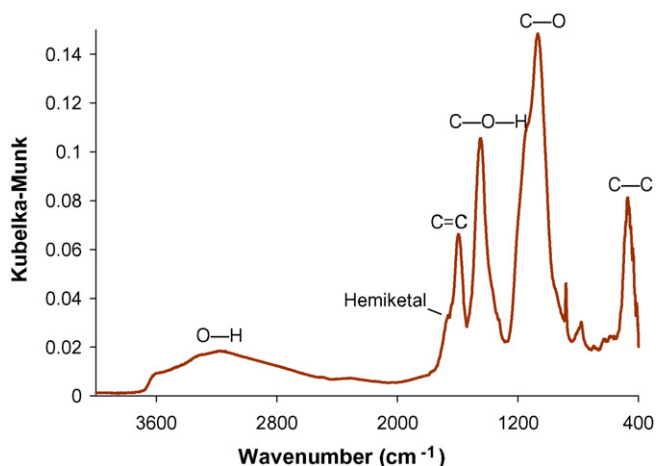


Fig. 1. FTIR spectrum of synthesized polyhydroxy fullerenes.

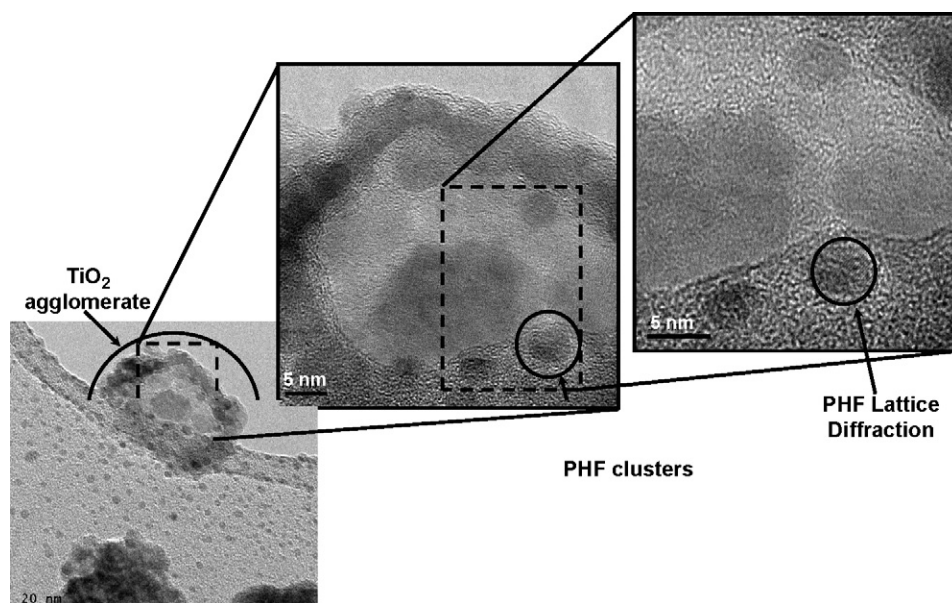


Fig. 3. HR-TEM images of PHF coated on TiO_2 nanoparticles.

3.3. EPR analysis

The EPR spectra obtained after UVA irradiation of DMPO and TiO_2 alone or TiO_2 + PHF (Fig. 4) were identical in terms of peak locations and the characteristic 1:2:2:1 relative peak magnitudes associated with trapped hydroxyl radicals in the form of DMPO–OH [19]. Presence of PHF in the reaction mixtures had no effect on peak locations, but substantially increased peak magnitudes. This shows that addition of PHF increases the concentration of DMPO–OH $^\bullet$, indicating higher rates of free hydroxyl radical generation.

Plots of the DMPO–OH $^\bullet$ concentrations achieved after UVA irradiation of various reaction mixtures is presented in Fig. 5. No production of DMPO–OH $^\bullet$ was observed in the dark control. A concentration of 1.2 μM DMPO–OH was formed in the UVA control over 60 min, corresponding to a yield of $0.33 \text{ M cm}^2 \text{ J}^{-1}$. This is comparable to the irradiated control yield of $0.5 \text{ M cm}^2 \text{ J}^{-1}$ obtained by Uchino et al. [19].

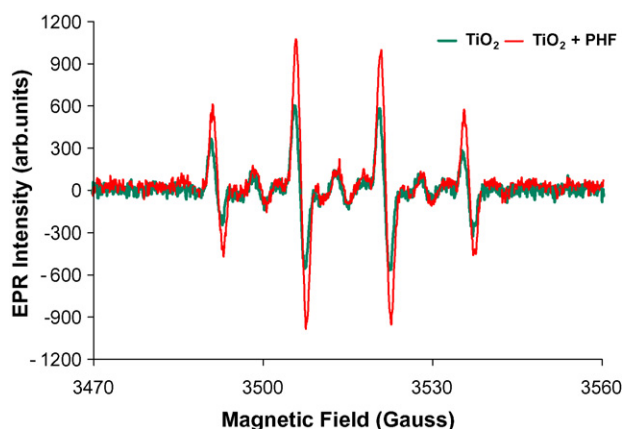


Fig. 4. EPR spectra obtained upon UVA irradiation of DMPO and TiO_2 alone or TiO_2 + PHF.

Production of DMPO–OH $^\bullet$ by irradiation of PHF alone was the same as in the UVA control, indicating that PHF alone does not generate hydroxyl radicals. Substantially higher DMPO–OH $^\bullet$ concentrations were obtained when TiO_2 was present in the reaction mixture, reflecting the contribution of photocatalysis. The rate of DMPO–OH $^\bullet$ production in the presence of both TiO_2 and PHF was in the range of 20–60% higher than the rate obtained with TiO_2 alone.

The concentration of DMPO–OH $^\bullet$ generated exhibits a maximum as a function of UVA irradiation time followed by a gradual decrease. Similar observations have been reported by others for ceria [25] and TiO_2 photocatalysts [26]. Such a relationship may be due to degradation of trapped radicals, accompanied by a drop-off in the rate of DMPO–OH $^\bullet$ production. DMPO–OH $^\bullet$ is known to be unstable, with a half-life of 20 min [27]. One possible mechanism of degradation is multiple additions of hydroxyl radicals on DMPO [26]. However, Hernandez-Alonso et al. [25] showed experimental

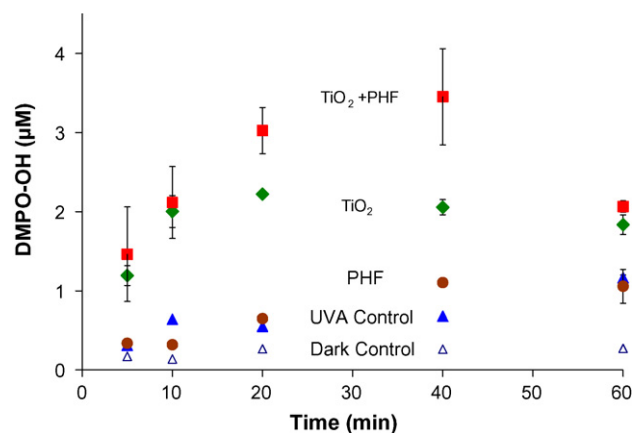


Fig. 5. Effect of PHF on generation of hydroxyl radicals by UVA irradiation of titanium dioxide.

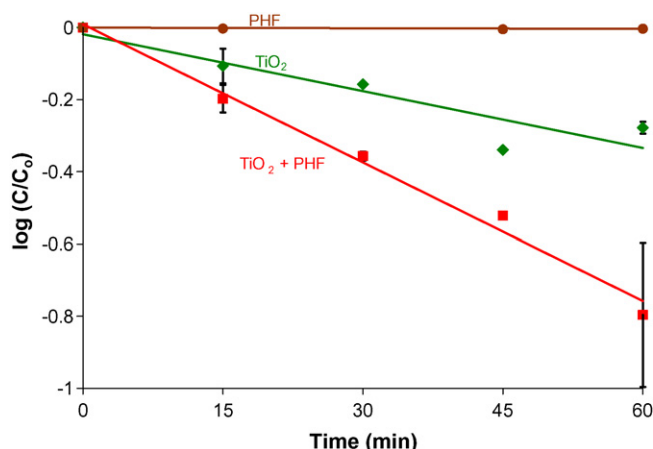


Fig. 6. First-order degradation kinetics of Procion Red MX-5B upon UVA irradiation with TiO_2 alone and $TiO_2 + PHF$. Error bars are ± 1.0 S.D.; some of the error bars are too small to be visible.

results that conflict with the multiple addition mechanism, and argued that direct oxidation of $DMPO-OH^\bullet$ radicals by photo-generated holes could better explain their results. A slow-down in the production rate of $DMPO-OH^\bullet$ could occur due to consumption of oxygen [28], resulting in accumulation of electrons thus promoting electron-hole recombination. Direct oxidation of $DMPO-OH^\bullet$ radicals by photogenerated holes would lead to a slow-down in free hydroxyl generation from holes and thus decreased $DMPO-OH^\bullet$ production.

3.4. Dye degradation

The photocatalytic degradation of the triazine monoazo compound Procion red MX-5B by irradiation with TiO_2 (anatase) in the presence and absence of PHF is presented in Fig. 6. Both reaction mixtures followed pseudo-first-order degradation kinetics as indicated by the linear fits obtained to semilog plots of normalized dye concentration versus time. The rate of degradation with PHF, as indicated by the slope of the fit, was significantly greater than the rate without PHF ($\alpha = 0.01$). The pseudo-first-order rate coefficient with PHF ($0.0128 \pm 0.0029 \text{ min}^{-1}$) was 2.6 times higher than the rate coefficient without PHF ($0.0048 \pm 0.0005 \text{ min}^{-1}$). It is noteworthy that the rate of dye degradation with PHF alone ($6 \times 10^{-5} \text{ min}^{-1}$) was two-orders of magnitude less than obtained with TiO_2 alone. This is consistent with the EPR results that indicate PHF itself does not generate hydroxyl radicals under UVA irradiation. Previous studies have reported that PHF can generate superoxide radicals with UVA and visible light [29–31]. However, the rate of generation of superoxide radicals is dependent on the pH; the rate at pH 7 ($9 \times 10^{-5} \text{ min}^{-1}$) is 100 times slower than at pH 5 [30]. In the present study, at pH 6, the generation of superoxide radicals may not be significant and therefore no dye degradation was observed.

3.5. Inactivation of *Escherichia coli*

Kinetics of the photocatalytic inactivation of *E. coli* are presented in Fig. 7. Inactivation rate in the absence of P25 (i.e.,

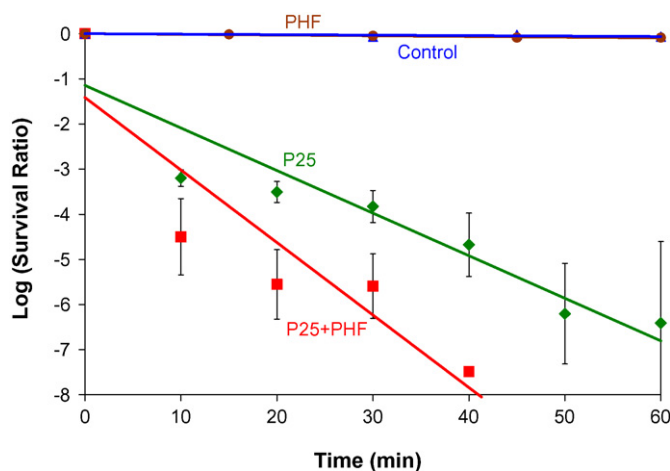


Fig. 7. Photocatalytic inactivation of *E. coli* plotted as a function of survival ratio vs. time. Error bars are ± 1.0 S.D.; error bars for PHF and control are too small to be visible.

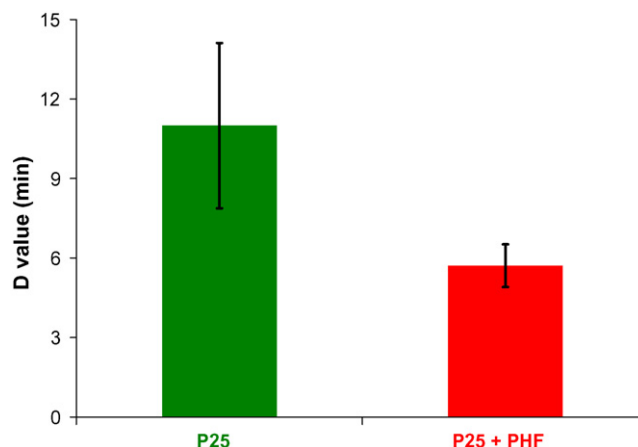


Fig. 8. *E. coli* inactivation with Degussa P25 alone and a mixture of Degussa P25 and PHF. Error bars are ± 1.0 S.D.

control and PHF alone) was essentially zero. The inactivation rate coefficient for P25 + PHF ($0.177 \pm 0.022 \text{ min}^{-1}$) is 1.9 times faster than the inactivation rate for P25 alone ($0.094 \pm 0.027 \text{ min}^{-1}$). Fig. 8 shows that the *D* value (time required for 1 log reduction of *E. coli*) with P25 + PHF is 7.1 min, which is significantly less ($\alpha = 0.05$) than the time of 11.7 min required with P25 alone. Complete destruction of *E. coli* is achieved in 40 min by P25 + PHF, compared to 60 min by P25 alone. These results are noteworthy, since P25 is the best commercially available photocatalyst. Furthermore, they indicate that the PHF is capable of enhancing the action of different photocatalysts, which suggests that the mechanism must be of a general nature, such as electron scavenging.

4. General discussion

The quite substantial degree of enhancement in photocatalysis achieved in the presence of PHF would seem to contradict previous literature. As previously discussed, free radical generation by PHF alone is orders of magnitude lower

than production by TiO₂ alone and is thus not responsible for the observed enhancement. This leaves electron scavenging by PHF as the most plausible explanation. In fact, fullerenes are well known as electron acceptors, but this property was reportedly lost upon hydroxylation by the acid synthesis route [32]. Notably, the PHF produced in this study through the alkali synthesis route have a higher number (36 versus 18) of functional groups and could thus possess different properties than the previously reported material.

PHF have also been reported to be radical scavengers. They are employed as antioxidants for therapeutic applications due to their ability to neutralize both hydroxyl and superoxide radicals [33–35]. Scavenging of these radicals might be expected to decrease, not increase the rate of photocatalysis. However, the lifetime of hydroxyl radicals is very short (20 ns, [27]), therefore only those radicals generated close to PHF could be scavenged. The surface coverage of TiO₂ by PHF at the concentrations used in the present study is less than a monolayer [14]. The potential for hydroxyl radical scavenging is therefore limited. Superoxide radicals have a longer lifetime and thus may diffuse to the PHF. However, PHF is adsorbed to the TiO₂ surface at the beginning of the experiment [14], presenting an immediate and direct route for electron transfer. Thus, it is likely that the preferred route of electron transfer to the PHF is directly from the TiO₂, rather than through the diffusion-mediated superoxide route.

The present study is in agreement with the hypothesis that PHF can scavenge the photo-generated electrons from TiO₂ and therefore increases the rate of hydroxyl radical generation. Addition of PHF to photocatalytic systems resulted in an enhancement of hydroxyl radical generation as demonstrated by EPR, inactivation of *E. coli* as well as dye degradation experiments. The enhancement (2.6×) with the synthesized batch of fullerenes is higher than previously reported by Krishna et al. The increase in enhancement could be due to difference in number and type of functional groups, in which case further optimization of functional groups is a plausible approach for achieving greater enhancement in photocatalysis.

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References

- [1] J. Arana, J.A.H. Melian, J.M.D. Rodriguez, O.G. Diaz, A. Viera, J.P. Pena, P.M.M. Sosa, V.E. Jimenez, Catal. Today 76 (2002) 279–289.
- [2] S.-S. Hong, M.S. Lee, S.S. Park, G.-D. Lee, Catal. Today 87 (2003) 99–105.
- [3] J. Matos, J. Laine, J.M. Herrmann, J. Catal. 200 (2001) 10–20.
- [4] R.M. Mohamed, A.A. Ismail, I. Othman, I.A. Ibrahim, J. Mol. Catal. A: Chem. 238 (2005) 151–157.
- [5] K.I. Shimizu, T. Kaneko, T. Fujishima, T. Kodama, H. Yoshida, Y. Kitayama, Appl. Catal. A: Gen. 225 (2002) 185–191.
- [6] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, J. Phys. Chem. 99 (1995) 9986–9991.
- [7] K. Tanaka, J. Fukuyoshi, H. Segawa, K. Yoshida, J. Hazard. Mater. 137 (2006) 947–951.
- [8] I.M. Arabatzis, T. Stergiopoulos, D. Andreeva, S. Kitova, S.G. Neophytides, P. Falaras, J. Catal. 220 (2003) 127–135.
- [9] T. Sreethawong, S. Yoshikawa, Catal. Commun. 6 (2005) 661–668.
- [10] V. Subramanian, E.E. Wolf, P.V. Kamat, Langmuir 19 (2003) 469–474.
- [11] B. Sun, A.V. Vorontsov, P.G. Smirniotis, Langmuir 19 (2003) 3151–3156.
- [12] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, J. Photochem. Photobiol. A: Chem. 148 (2002) 233–245.
- [13] C. Wang, T.M. Wang, S.K. Zheng, Physica E 14 (2002) 242–248.
- [14] V. Krishna, N. Noguchi, B. Koopman, B. Moudgil, J. Colloid Interf. Sci. 304 (2006) 166–171.
- [15] V. Krishna, S. Pumprueg, S.H. Lee, J. Zhao, W. Sigmund, B. Koopman, B.M. Moudgil, Process Safety Environ. Protection 83 (2005) 393–397.
- [16] Y. Yu, J.C. Yu, J.G. Yu, Y.C. Kwok, Y.K. Che, J.C. Zhao, L. Ding, W.K. Ge, P.K. Wong, Appl. Catal. A: Gen. 289 (2005) 186–196.
- [17] J. Li, A. Takeuchi, M. Ozawa, X.H. Li, K. Saigo, K. Kitazawa, J. Chem. Soc. – Chem. Commun. (1993) 1784–1785.
- [18] A.G. Rincon, C. Pulgarin, Appl. Catal. B: Environ. 44 (2003) 263–284.
- [19] T. Uchino, H. Tokunaga, M. Ando, H. Utsumi, Toxicol. In Vitro 16 (2002) 629–635.
- [20] L.O. Husebo, B. Sitharaman, K. Furukawa, T. Kato, L.J. Wilson, J. Am. Chem. Soc. 126 (2004) 12055–12064.
- [21] B. Vilen, P.R. Marcoux, M. Lekka, A. Sienkiewicz, T. Feher, L. Forro, Adv. Funct. Mater. 16 (2006) 120–128.
- [22] G.M. Xing, et al. J. Phys. Chem. B 108 (2004) 11473–11479.
- [23] L.Y. Chiang, R.B. Upasani, J.W. Swirczewski, S. Soled, J. Am. Chem. Soc. 115 (1993) 5453–5457.
- [24] R.M. Silverstein, F.X. Webster, Spectrometric Identification of Organic Compounds, Wiley, New York, 1998.
- [25] M.D. Hernandez-Alonso, A.B. Hungria, A. Martinez-Arias, M. Fernandez-Garcia, J.M. Coronado, J.C. Conesa, J. Soria, Appl. Catal. B: Environ. 50 (2004) 167–175.
- [26] D. Dvoranova, V. Brezova, M. Mazur, M.A. Malati, Appl. Catal. B: Environ. 37 (2002) 91–105.
- [27] M.A. Grela, M.E.J. Coronel, A.J. Colussi, J. Phys. Chem. 100 (1996) 16940–16946.
- [28] V. Brezova, A. Stasko, L. Lapcik, J. Photochem. Photobiol. A: Chem. 59 (1991) 115–121.
- [29] J.P. Kamat, T.P.A. Devasagayam, K.I. Priyadarsini, H. Mohan, Toxicology 155 (2000) 55–61.
- [30] K.D. Pickering, M.R. Wiesner, Environ. Sci. Technol. 39 (2005) 1359–1365.
- [31] B. Vilen, A. Sienkiewicz, M. Lekka, A.J. Kulik, L. Forro, Carbon 42 (2004) 1195–1198.
- [32] H. Mohan, L.Y. Chiang, J.P. Mittal, Res. Chem. Intermed. 23 (1997) 403–414.
- [33] G. Bogdanovic, V. Kojic, A. Dordevic, J. Canadanovic-Brunet, M. Vojinovic-Miloradov, V.V. Baltic, Toxicol. In Vitro 18 (2004) 629–637.
- [34] A. Djordjevic, J.M. Canadanovic-Brunet, M. Vojinovic-Miloradov, G. Bogdanovic, Oxid. Commun. 27 (2004) 806–812.
- [35] S.M. Mirkov, A.N. Djordjevic, N.L. Andric, S.A. Andric, T.S. Kostic, G.M. Bogdanovic, M.B. Vojinovic-Miloradov, R.Z. Kovacevic, Nitric Oxide – Biol. Chem. 11 (2004) 201–207.